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(19)

(54) AN AQUEOUS PIGMENT SUSPENSION

(71) We, BAYER AKTIENGESELLSCHAFT a body corporate organised under the laws of the Federal Republic of Germany of 509 Leverkusen, Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to an aqueous pigment suspension and in particular to a titanium dioxide pigment suspension and to a process for its preparation.

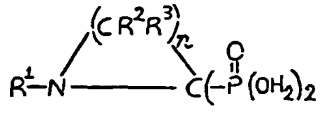
Pigments are widely used and processed in the form of aqueous suspensions. Examples are the manufacture of pigmented paper, in which anatase is added to an aqueous suspension of cellulose fibres and the pulp is formed into a paper sheet on a sieve after the addition of auxiliary agents such as flocking agents, or the manufacture of disperse dyes in which titanium dioxide pigments may be added to an aqueous synthetic resin dispersion in addition to fillers such as silicates, chalk and heavy spar, etc., Pigment suspensions of this kind are also important where spray drying processes are carried out, e.g. following an after-treatment of titanium dioxide pigments, for example, with SiO_2, Al_2O_3 or TiO_2. Suspensions used with this method of drying must have as low a water content as possible for economical reasons but they must still be fluid.

To facilitate the use of the pigment in aqueous suspensions by the consumer, it has become customary to market the pigments in the form of highly concentrated aqueous suspensions (from 50% to 75% by weight) instead of as dry powders. When preparing such suspensions, it is aimed to keep their water content as low as possible in order to achieve optimum utilisation of the storage and transport space. However, such pigment suspensions having a high solid content are very highly viscous and tend to thicken in storage so that the suspensions become difficult to use. It has therefore become customary to treat the suspensions with certain additives which reduce their viscosity and prevent thickening. α-Aminoalkylene diphosphonic acids have already been proposed as such additives, e.g. phenylaminomethylene diphosphonic acid (German Offenlegungsschrift No. 1,542,202, US Patent Specification No. 3,713,859).

However, pigment suspensions of this kind, as a rule, still have too high a viscosity or else a relatively limited storage life.

We have sought to obviate or at least substantially to reduce the disadvantages which occur in known pigment suspensions.

Accordingly, the present invention provides aqueous pigment suspensions which contain at least one aminophosphonic acid of the general formula (I)



(I)

and/or salt thereof,
in which formula

R^1, R^2 and R^3 denote, independently of each other, hydrogen or an alkyl group having from 1 to 3 carbon atoms and

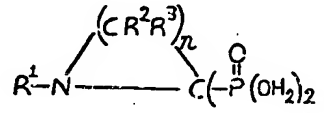
n has a value of from 3 t 11.

The aqueous pigment suspension according to the invention has a high solid content and is exceptionally stable in storage.

The concentration of these additives is preferably from 0.01 to 1% by weight, based on the solid content of the pigment suspensions, more preferably from 0.05 to 0.05% by weight and most preferably from 0.1 to 0.3% by weight.

The aqueous pigment suspension may contain, for example, from 50% to 75% by weight of pigment.

The present invention also provides a process for the preparation of an aqueous pigment suspension wherein at least one aminophosphonic acid of the general formula (I)



(I)

and/or at least one salt thereof wherein

R^1, R^2 and R^3 denote, independently of each other, hydrogen or an alkyl group having from 1 to 3 carbon atoms and

n has a value of from 3 to 11

is mixed with a pigment before, during or after suspension of the pigment and wherein the pH is adjusted to within a pH range of from 5 to 12.

Aminophosphonic acids of the general formula (I) wherein $n \leqq 5$ are already known from German Offenlegungsschrift No. 2,343,196.

It was surprising to find that the special aminophosphonic acids corresponding to the general formula (I) which are azacycloalkane diphosphonic acids show a substantially better effect than aminophosphonic acids of the kind described, for example, in German Offenlegungsschrift No. 1,542,202 or in US Patent Specification No. 3,713,859.

Pigment suspensions prepared according to the invention are distinguished from known pigment suspensions having the same solid content by their lower viscosity and improved stability in storage. Another advantage is that the phosphonic acids required as additives can easily be prepared and in high yields from relatively simple, readily available starting materials. Furthermore, fluctuations in the properties of the pigments within the usual tolerances have a less pronounced effect in the pigment suspensions according to the invention than in pigment suspensions prepared according to the prior art.

The present invention is suitable for inorganic pigments such as SiO_2, FeOOH, Fe_3O_4, Cr_2O_3 or TiO_2. Particularly advantageous results are obtained with titanium dioxide pigments such as rutile or anatase. The titanium dioxide pigments may be subjected to inorganic or organic after-treatments. Known inorganic after-treatment of TiO_2 pigments consists, for example, of enveloping them with SiO_2 Al_2O_3, TiO_2, ZrO_2, ZnO, MgO and/or phosphates. Organic after-treatment with amines, hydroxyalkanes, epoxides, etc. also in no way impairs the preparation of the pigment suspensions. The titanium dioxide used according to the present invention may be worked up either by the chloride process or by the sulphate process.

The following are examples of diphosphonic acids which may be used: Azacycloheptane (2,2) diphosphonic acid, azacyclopentane (2,2) diphosphonic acid, N-methylazacyclopentane (2,2) diphosphonic acid, 7-methylazacycloheptane (2,2) diphosphonic acid, and azacyclotridecane (2,2) diphosphonic acid. Neutral and acid salts of diphosphonic acid may also be used. Suitable cations for this purpose include, for example, sodium, lithium, potassium, magnesium, ammonium, hydrazinium, hydroxyl ammonium and primary, secondary, tertiary and quaternary ammonium ions. Apart from the acids mentioned above, their monoammonium salts are also particularly preferred additives according to the present invention.

The pigment suspensions may contain the usual auxiliary substances such as cellulose ethers, sorbitol, etc., fillers such as heavy spar, chalk, silicates or silicic acids, dolomite or mica and preservatives such as para-chlorometacresol and sodium pentachlorophenolate, etc. These auxiliary substances are generally used in quantities of from 0.05 to 5% by weight, based on the pigment suspension. The pigment suspensions are advantageously prepared by introducing into the reaction vessel the quantity of water required for obtaining the desired solid content (e.g. 70%) and then adding the liquefying additives before adjusting the pH to a value of from 8 to 9 by the addition of sodium hydroxide solution or some other alkaline liquor and finally adding the pigment with stirring.

Alternatively, the pigment may be mixed stepwise with the required quantity of water with the aid f a high speed stirrer which produces high turbulence (e.g. a propeller stirrer) so that a mash is formed to which the liquefying additives are introduced stepwise as the mash thickens until the mixture c ntains the required percentage of solid matter and liquefying agent. Pigment suspensions which have already solidified (e.g. filter cakes) can be liquefied in analogous manner by vigorous mixing (e.g. kneading) with the liquefying additives according to the invention.

The pigment suspensions according to the invention may be dried and milled. The resulting pigment powders may be reliquefied with water in a single operation to produce high percentage pigment suspensions. Dry pigment powders may be treated in analogous manner by mixing or milling them in the solid state with the additives which are suitable for liquefaction according to the invention, and the resulting mixture may then be stirred with water to form a high percentage pigment suspension.

The present invention will now be illustrated by the following Examples in which the percentages are specified on a weight basis:

Example 1.

Preparation of various highly concentrated anatase suspensions using azacycloheptane (2,2) diphosphonic acid and, as comparison substance, phenylaminomethylene diphosphonic acid.

The TiO_2 pigment used was a commercial product consisting of untreated anatase with a TiO_2 content of 99%. The quantity of wetting agent was 0.1%, based on the quantity of pigment. Azacycloheptane (2,2)-diphosphonic acid (No. 1) used as wetting agent was compared with phenylamino methylene diphosphonic acid (No. 2) and its sodium salts.

The anatase suspensions or slurries were prepared by first introducing into the reaction vessel the quantity of water required for obtaining the desired solid content (68%, 70% and 72%). When preparing the slurries of untreated anatase (Examples 1 to 3), distilled water was used for the sake of better reproducibility. Ordinary tap water was used for the other examples. The pH was adjusted to 8—9 with NaOH after the required quantity of additive had been introduced into the water. The quantity of anatase required for obtaining the necessary solid content was then added continuously with stirring. Finally, when all the pigment had been introduced into the suspension, it was dispersed at the optimum speed of rotation for about 20 minutes.

The viscosities were measured (seconds), where possible using DIN 4- or DIN 6-cups. This method at the same time demonstrates very clearly the flow properties of the suspensions. In addition, the viscosities (Pa.s) were determined with the aid of a rotation viscosimeter (Rheomat 15 of Contraves, Switzerland), if possible at the same shear velocity or at the highest possible shear velocity (D/sec^{-1}).

Additives	Solid Content (%)	Viscosity in Rheomat 15 $D(sec^{-1})$	(Pa.s)	$D(sec^{-1})$	(Pa.s)	DIN 4 Cup (sec)	DIN 6 (sec)
No. 1	68	84.5	0.089	195.7	0.059	13.5	5.7
	70	84.5	0.15	195.7	0.094	15.0	6.0
	72	84.5	0.24	195.7	0.13	19.5	6.3
No. 2	68	74.48	15.7	98.3	13.8	nm	nm
	70	74.48	15.7	98.3	19.6	nm	nm
	72	79.37	21.1	98.3	19.7	nm	nm

nm=not measurable

Example 2.

Influence of the quantity of wetting agent on the viscosity and fluidity of a 72% anatase suspension when using azacycloheptane (2,2)-diphosphonic acid (No. 1) and phenylaminomethylene diphosphonic acid (No. 2).

Preparation of the suspensions was carried out as in Example 1. The solid content (72%) of the suspensions was kept constant while the quantity of additive was varied. Measurement of the fluidity or viscosity was also carried out as described in Example 1.

Additive	Quantity used (%)	Solid content (%)	Viscosity in Rheomat 15 D (sec^{-1})	(Pa.s)	DIN 4 Cup (sec)
No. 1	0.0	72	98.3	20.7	nm
	0.05	72	84.5	0.28	24.9
	0.1	72	84.5	0.27	24.3
	0.15	72	84.5	0.28	23.1
	0.2	72	84.5	0.32	22.6
	0.3	72	84.5	0.46	33.0
No. 2	0.05	72	79.37	21.3	nm
	0.1	72	79.37	19.5	nm
	0.15	72	79.37	17.5	nm
	0.2	72	79.37	16.8	nm
	0.3	72	79.37	19.3	nm

Example 3.

Preparation of highly concentrated anatase suspensions with 0.3% of additive.

Preparation and measurement of the suspensions was carried out as described in Example 1. When using azacycloheptane (2,2)-diphosphonic acid (No. 1), methylazacycloheptane (2,2)-diphosphonic acid (No. 3) and azacyclotridecane (2,2)-diphosphonic acid (No. 4), the maximum concentration of anatase pigment (described in Example 1) which could be obtained in suspensions which were still fluid was 72% and 75%, respectively. When aminotrimethylenephosphonic acid (comparison substance No. 5) was used, the highest concentration obtainable in suspensions which were still readily fluid was only 58%. When the solid content was increased to 60% and 62%, the suspensions were already slightly pasty.

Additives	Solid content (%)	Viscosity in Rheomat 15 D(sec^{-1})	(Pa.s)	DIN 4 Cup (sec)	DIN 6 Cup (sec)
No. 1	72	84.5	0.45	36.0	9.0
	75	77.92	1.15	nm	nm
No. 3	72	77.92	0.43	12.0	5.4
	75	84.5	0.44	36.3	9.0
No. 4	72	77.92	0.69	nm	nm
	75	77.92	0.87	nm	nm
No. 5	58	84.5	0.024	15.6	6.0
	60	98.3	1.25	nm	nm
	62	98.3	2.14	nm	nm

Example 4.

Preparation of a 75% suspension of an after-treated anatase pigment with the aid of azacycloheptane (2,2)-diphosphonic acid (No. 1) and aminotrimethylene-phosphonic acid (No. 5).

Preparation and measurement of the suspensions was carried ut as described in Example 1 except that the pigment used in this case was a commercial micronised anatase pigment which had been after-treated with aluminium oxide and an organic substance. The pigment has a TiO_2 content of 96%. Various quantities of additives were used.

Additives	Quantity used (%)	Solid content (%)	Viscosity in Rheomat 15 D(sec^{-1})	(Pa.s)
No. 1	0.0	75	31.6	47.0
	0.1	75	137.5	0.39
	0.2	75	137.5	0.63
	0.3	75	137.5	0.64
	0.4	75	137.5	0.64
No. 2	0.1	75	137.5	1.08
	0.2	75	137.5	1.14
	0.3	75	137.5	1.42
	0.4	75	137.5	1.40

Example 5.

Preparation of a rutile suspension using two differently after-treated rutile pigments and azacycloheptane (2,2)-diphosphonic acid (No. 1), methylazacyclo-heptane (2,2)-diphosphonic acid (No. 3), azacyclotridecane (2,2)-diphosphonic acid (No. 4) and aminotrimethylene phosphonic acid (No. 5).

Preparation and measurement of the suspensions was carried out as described in Example 1. Rutile 1 was a commercial micronised rutile pigment which had been after-treated with aluminium and silicon compounds and stabilized with zinc oxide. Rutile 2 differed from rutile 1 only in that it had been after-treated with aluminium compounds alone. Both pigments were in addition organically treated, in each case 0.1% of additives (based on the quantity of pigment) was used.

Additives	Solid cont. (%)	Additives No. 1 D(sec^{-1})	(Pa.s)	No. 3 D(sec^{-1})	(Pa.s)	No. 4 D(sec^{-1})	(Pa.s)	No. 5 D(sec^{-1})	(Pa.s)
Rutile 1	72	195.7	0.044	195.7	0.06	195.7	0.005	195.7	0.124
Rutile 2	75	195.7	0.164	195.7	0.155	137.1	0.19	137.1	0.314

Example 6.

Preparation of a suspension of two commercial iron oxide black pigments (Fe_3O_4) using the additives mentioned in Example 5. Method of preparing and examining the suspensions as described in Example 1.

Pigment	Solid content (%)	D(sec^{-1})	Additive (01.% based on quantity of pigment) No. 1 (Pa.s)	No. 3 (Pa.s)	No. 4 (Pa.s)	No. 5 (Pa.s)
Fe_3O_4	65	98.3	2.09	2.98	2.11	2.97
Fe_3O_4	62	98.3	2.22	1.87	2.61	3.08

Example 7.

Preparation of a suspension of two commercial iron oxide red pigments. Fe_2O_3 is a micronised pigment. The suspensions were prepared and examined as in Example 1.

Pigment	Solid content (%)	D(sec^{-1})	Additive (0,1%) No. 1 (Pa.s)	No. 3 (Pa.s)	No. 4 (Pa.s)	No. 5 (Pa.s)
Fe_2O_3 1	70	195.7	0.063	0.067		0.122
Fe_2O_3 2	70	98.3	2.31	1.97		3.22

Example 8.

Preparation of a suspension of a commercial micronised iron yellow pigment: (FeOOH).

Pigment	Solid content (%)	D(sec^{-1})	Additives (0.1%) No. 1 (Pa.s)	No. 3 (Pa.s)	No. 4 (Pa.s)	No. 5 (Pa.s)
FeOOH	42	98.3	3.84	3.34	3.64	6.34

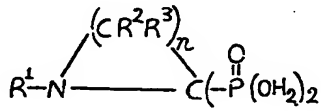
Example 9.

Preparation of a suspension of commercial chromium oxide pigment (Cr_2O_3).

Pigment	Solid content (%)	No. 1 D(sec^{-1})	(Pa.s)	Additive No. 3 D(sec^{-1})	(Pa.s)	No. 5 D(sec^{-1})	(Pa.s)
Cr_2O_3	75	195.7	0.491	137.1	0.335	98.3	2.51

WHAT WE CLAIM IS:—

1. An aqueous pigment suspension containing at least one aminophosphonic acid of the general formula (I)



(I)

and/or at least one salt thereof, in which formula R^1, R^2 and R^3 denote, independently of each other, hydrogen or an alkyl group having from 1 to 3 carbon atoms and n has a value of from 3 to 11.

2. An aqueous pigment suspension according t claim 1, which c ntains 0.01 to

1% by weight of the aminophosphonic acid and/or salt based n the solid content of the pigment suspension.

3. An aqueous pigment suspension according to claim 2, which contains 0.05 to 0.5% by weight of the aminophosphonic acid and/or salt, based on the solid content of the pigment suspension.

4. An aqueous pigment suspension according to claim 3, which contains 0.1 to 0.3% by weight of the aminophosphonic acid and/or salt, based on the solid content of the pigment suspension.

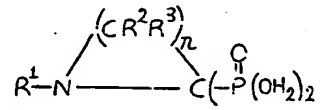
5. An aqueous pigment suspension according to any of claims 1 to 4, which contains from 50% to 75% by weight of pigment.

6. An aqueous pigment suspension according to any of claims 1 to 5, which contains one or more of sodium, lithium, potassium, magnesium, ammonium, hydrazinium, hydroxyl ammonium or alkyl ammonium salts of the aminophosphonic acid of general formula (I).

7. An aqueous pigment suspension according to any of claims 1 to 6, which contains titanium dioxide pigment.

8. An aqueous pigment suspension according to claim 1 substantially as herein described with reference to any of the specific Examples.

9. A process for the preparation of an aqueous pigment suspension which contains at least one aminophosphonic acid and/or at least one salt thereof, wherein at least one aminophosphonic acid of the general formula (I)



(I)

and/or at least one salt thereof,
in which formula R^1, R^2 and R^3 denote, independently of each other, hydrogen or an alkyl group having from 1 to 3 carbon atoms and $n=3$ to 11,
is mixed with a pigment before, during or after suspension of the pigment in water and wherein the pH is adjusted to within a pH range of from 5 to 12.

10. A process according to claim 9 substantially as herein described with reference to any of the specific Examples.

11. An aqueous suspension when prepared by a proccess as claimed in claim 9 or 10.

12. A pigmented paper comprising a pigment derived from an aqueous pigment suspension according to any of claims 1 to 8 and 11.

13. An aqueous synthetic resin dispersion comprising a pigment suspension according to any of claims 1 to 8 and 11.

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